JOURNAL OF MAGNETIC RESONANCE 8, 354–365 (1972)

Quantitative Aspects of Coherent Averaging. Simple Treatment of Resonance Offset Processes in Multiple-Pulse NMR*

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Received January 28, 1972

A simple zero-order treatment of averaging by resonance offset fields in multiple-pulse NMR is presented. If the resonance offset is smaller than the inverse rf cycle time but larger than the local fields, then the average dipolar Hamiltonian has the same form as the truncated dipolar Hamiltonian in the rotating frame, and is scaled by an easily calculated factor. From this fact, several general conclusions are drawn and the possibility of line narrowing, spin locking and time reversal is discussed for several pulse sequences. For the phase-alternated two-pulse sequence it is demonstrated explicitly by a calculation of truncated second moments that behavior at and far from resonance should be radically different, indicating that caution should be exercised in the analysis of such experiments.

INTRODUCTION

The problem of calculating the response of a coupled spin system to an arbitrary radiofrequency excitation is, in general, an extremely complex one. It is well known, however, that if the excitation fulfils certain conditions of periodicity and duration, an enormous simplification ensues, taking the form of what we have called "coherent averaging" (*1*). This theory has formed a powerful tool for the description and design of a variety of effects in pulsed NMR, including spin locking (*2–4*), line narrowing and high resolution NMR in solids (*5–7*), spin echoes (*8*), steady-state behavior (*9*), and scaling of inhomogeneous shifts (*10*).

It was noticed in several of these experiments that when pulse trains were applied with the rf carrier frequency substantially displaced from the Larmor frequency of the spin system, i.e., with a "resonance offset," a new phenomenon manifested itself in the form of additional averaging, for example enhanced line narrowing. This phenomenon has recently been explained and, in fact, has been shown to possess a number of useful properties (*11*).

Basically, what happens, in qualitative terms, is the following: in the presence of rf excitation the coupling between the spins becomes modulated with a period equal to that of the excitation itself, in an appropriate reference frame (*1*, *12*). In the limit of strong modulation we perform a time average of this time-dependent coupling and obtain an average coupling which effectively governs the response of the spin system.

* This work was supported in part by the National Institutes of Health and in part by the National Science Foundation.

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The process of "truncation" of the dipolar interaction in the presence of a large static external field (*13–16*), for example, is a particular case of this approach (*11*). Now, consider what happens if there is a large resonance offset. In the rotating frame, this appears as a static magnetic field and, as in the case of truncation just mentioned, this field will provide an additional modulation of the coupling, which may be averaged in the appropriate limit (*1*). Thus, the behavior of pulsed NMR experiments near and far from resonance should be distinctly different, as has indeed been observed (*11*).

In this communication, we wish to present a simple treatment of this phenomenon in a form more amenable to an intuitive understanding and quantitative application to a variety of NMR experiments than that of our previous work. This presentation is warranted by the fact that these multiple-pulse techniques are becoming increasingly useful in studies of chemical problems, and resonance offset effects form an integral component in their usefulness and in their understanding.

The approach here is simple in the sense that only zero-order (*1*) averaging effects are considered, and insofar as is possible, the notation and tools used should be quite familiar. Higher-order effects are more conveniently treated in terms of irreducible tensor operators, since we are interested in the transformations of such operators under the rotations induced by the rf excitation. This will be deferred to a later detailed exposition of these experiments.

In section II a brief review of pertinent theory is presented and a general description of averaging due to resonance offset fields is derived. In section III this is applied to some simple multiple-pulse sequence and some of its uses and limitations are discussed. Details on the exact steps involved in the calculations of average Hamiltonians in various representations are not given, since this has been presented several times. The procedure is simply mentioned and the results written down directly. A concise review may be found in a forthcoming treatise on "magic-angle" experiments (*7*).

GENERAL THEORY

Hamiltonian and Frame of Reference

We begin by writing down a Hamiltonian for the system. We select as an example of a spin coupling the dipolar interaction, since this is the most important and widely encountered for solids of interest to chemists. The results are easily generalized, as we shall see. We write the Hamiltonian in the laboratory frame in frequency units:

$$\mathscr{H}_L(t) = \mathscr{H}_0 + \mathscr{H}_1(t) + \mathscr{H}_d. \qquad [1]$$

$\mathscr{H}_0$ is the Zeeman interaction with applied static field along the z axis

$$\mathscr{H}_0 = -\omega_0 I_z. \qquad [2]$$

$\mathscr{H}_1(t)$ the applied rf excitation

$$\mathscr{H}_1(t) = -2\omega_1(t) I_x \cos[\omega t + \phi(t)], \qquad [3]$$

where $\omega_1(t)$ and $\phi(t)$ describe the amplitude and phase modulation of the rf excitation applied at frequency ω, and

$$\mathscr{H}_d = -\sum_{i<j} \frac{\gamma^2 \hbar}{r_{ij^3}} \left[\frac{3(\boldsymbol{I}_i \cdot \boldsymbol{r}_{ij})(\boldsymbol{I}_j \cdot \boldsymbol{r}_{ij})}{r_{ij^2}} - \boldsymbol{I}_i \cdot \boldsymbol{I}_j \right] \qquad [4]$$

is the dipolar interaction.

We now perform the customary transformation to a coordinate system rotating at frequency ω about the z axis. An average is then performed over a time period of $2\pi/\omega$ and this removes the time-dependent terms in $\mathscr{H}_1(t)$ and $\mathscr{H}_d$ in this frame. All this is well known; it corresponds to discarding the counter-rotating component of the rf field and the nonsecular terms of the dipolar interaction (or truncation) and is just a special case of coherent averaging. It is clearly legitimate whenever $\mathscr{H}_0$ is much larger than $\mathscr{H}_1$ and $\mathscr{H}_d$. Our Hamiltonian in the rotating frame thus assumes the form

$$\mathscr{H}_R^0(t) = \mathscr{H}_\Delta + \mathscr{H}_1(t) + \mathscr{H}_D^0, \tag{5}$$

where R indicates the rotating frame.

$\mathscr{H}_\Delta$ is the resonance offset:

$$\mathscr{H}_\Delta = -\Delta\omega I_z; \qquad \Delta\omega = (\omega_0 - \omega) \tag{6}$$

$$\mathscr{H}_1(t) = -\boldsymbol{\omega}_1(t)\cdot\boldsymbol{I}, \tag{7}$$

$$\mathscr{H}_d^0 = \sum_{i<j} b_{ij}(3I_{iz}I_{jz} - \boldsymbol{I}_i\cdot\boldsymbol{I}_j); \qquad b_{ij} = \frac{-\gamma^2\hbar}{r_{ij}^3}P_2(\cos\theta_{ij}). \tag{8}$$

The form of $\boldsymbol{\omega}_1(t)$ depends on the particular experiment at hand. Note that for brevity we sometimes use the same notation for terms of $\mathscr{H}$ in different frames, to conform with accepted practice—the frame will always be specified if this is done. The ^{0} superscript indicates a truncation or zero-order average of the particular term.

If the spin system is initially described in the rotating frame by the density matrix $\rho_R(0) = \rho_L(0)$, then at time t it has evolved to a state described by

$$\rho_R(t) = U_R^0(t,0)\,\rho_R(0)\,U_R^{0\dagger}(t,0), \tag{9}$$

here $U_R^0(t,0)$ is the effective time development operator in the rotating frame, given by

$$U_R^0(t,0) = T\exp\left[-i\int_0^t \mathscr{H}_R^0(t')\,dt'\right] \tag{10}$$

and T is a time-ordering operator. It is an expansion of U in which we shall be interested.

Coherent Averaging Effects

We now prepare to take account of the modulation that the first two terms in Eq. [5] produce in the third. To this end we assume:

(i) $\mathscr{H}_1(t)$ is cyclic and periodic with period t_c, and t is restricted to integer values of t_c, $t = Nt_c$

(ii) $t_c \ll t_\Delta, T_2; t_\Delta = 2\pi/\Delta\omega,$ [11]

(i) has been discussed in detail (*1*) and (ii) will allow us to perform a factorization of [10] in two steps (*11*). Employing the conditions above we obtain to a good approximation factoring out $\mathscr{H}_1(t)$ in a straightforward application of the theory:

$$U_R^0(t,0) = \bar{U}_{TR}^0(t,0) = \exp(-it\bar{\mathscr{H}}_{TR}^0), \tag{12}$$

where

$$\bar{\mathscr{H}}^0_{TR} = \frac{1}{t_c}\int_0^{t_c} U_1^\dagger(t,0)\,[\mathscr{H}^0_d + \mathscr{H}_\Delta]\,U_1(t,0)\,dt$$

$$= \bar{\mathscr{H}}^0_d + \bar{\mathscr{H}}_\Delta = \bar{\mathscr{H}}^0_d - \overline{\Delta\omega} I_{\bar{\mu}}; \qquad U_1(t,0) = T\exp\left[-i\int_0^t \mathscr{H}_1(t')\,dt'\right]. \quad [13]$$

Note that restriction [11(i)] applies only to calculations involving time evolution as in Eq. [12] and not, of course, to calculations of expansion terms as in Eq. [13]. $\bar{\mathscr{H}}^0_{TR}$ is the average Hamiltonian; T stands for "toggling" (*12*) since $\bar{\mathscr{H}}^0_{TR}$ is precisely the average Hamiltonian in an interaction (toggling) frame defined by $\mathscr{H}_1(t)$; (due to restriction 11(i), $\bar{U}^0_{TR}$ is thus the effective evolution operator in the rotating frame). $\bar{\mu}$ refers symbolically to the average direction $\bar{\boldsymbol{\mu}}$ in the rotating frame along which the spins are quantized (*12*). This is easily visualized by taking a unit spin vector $\boldsymbol{\mu}$ along the z axis and applying $\mathscr{H}_1(t)$ in the rotating frame. Then we define:

$$\bar{\boldsymbol{\mu}} = \frac{\int_0^{t_c} U_1^\dagger(t,0)\,\boldsymbol{\mu} U_1(t,0)\,dt}{\left|\int_0^{t_c} U_1^\dagger(t,0)\,\boldsymbol{\mu} U_1(t,0)\,dt\right|}. \quad [14]$$

For example if $\boldsymbol{\omega}_1(t)$ consists of 90° phase-alternated δ-pulses along the x axis then $\bar{\boldsymbol{\mu}} = (1/\sqrt{2})(\boldsymbol{j} + \boldsymbol{k})$. This is illustrated in Fig. 1. $\overline{\Delta\omega}$ is analogously the average resonance offset over this cycle:

$$\overline{\Delta\omega} = \frac{\Delta\omega}{t_c}\left|\int_0^{t_c} \boldsymbol{\mu}(t)\,dt\right|. \quad [15]$$

We now add to [11] (i)–(ii) the further restriction:

$$\text{(iii)}\quad t_{\bar{\Delta}} \ll T_2; \qquad t_{\bar{\Delta}} = 2\pi\overline{\Delta\omega}^{-1}. \quad [11]$$

This allows us, exactly as above, to factor the operator in [12] and then take an average over one cycle of the interaction with the static field $-\overline{\Delta\omega} I_{\bar{\mu}}$. What we are doing is in fact a truncation of the average dipolar interaction $\bar{\mathscr{H}}^0_d$ due to the presence of a large static field along the $\bar{\mu}$ axis. To a good approximation then:

$$\bar{U}^0_{TR}(t,0) = \bar{U}_\Delta(t,0)\,\bar{U}^{00}_{DTR}(t,0), \quad [16]$$

where

$$\bar{U}_\Delta(t,0) = \exp(-it\bar{\mathscr{H}}_\Delta) \quad [17]$$

$$\bar{U}^{00}_{DTR}(t,0) = \exp(-it\bar{\mathscr{H}}^{00}_{DTR}) \quad [18]$$

$$\bar{\mathscr{H}}^{00}_{DTR} = \bar{\mathscr{H}}^{00}_d = \frac{1}{t_{\bar{\Delta}}}\int_0^{t_{\bar{\Delta}}} \bar{U}^\dagger_\Delta(t,0)\,\bar{\mathscr{H}}^0_d\,\bar{U}_\Delta(t,0)\,dt. \quad [19]$$

Here the additional D subscript stands for "doubly rotating"—$\bar{\mathscr{H}}^{00}_{DTR}$ is precisely the average Hamiltonian in a frame which now rotates about the $\bar{\mu}$ axis at frequency $\overline{\Delta\omega}$ (*12*). Superscript ^{00} indicates the double averaging or truncation.

Now using Eqs. [13] and [19] and changing the order of integration over t_c and $t_{\bar{\Delta}}$ we have

$$\bar{\mathscr{H}}^{00}_{DTR} = \frac{1}{t_c t_{\bar{\Delta}}} \int_0^{t_c} dt'' \int_0^{t_{\bar{\Delta}}} dt' \, \bar{U}^{\dagger}_{\Delta}(t',0)\, U^{\dagger}_1(t'',0)\, \mathscr{H}^0_d\, U_1(t'',0)\, \bar{U}_{\Delta}(t',0), \qquad [20]$$

but using [13] and [17] it is easily found that

$$\frac{1}{t_{\bar{\Delta}}} \int_0^{t_{\bar{\Delta}}} dt' \, \bar{U}^{\dagger}_{\Delta}(t',0)\, U^{\dagger}_1(t'',0)\, \mathscr{H}^0_d\, U_1(t'',0)\, \bar{U}_{\Delta}(t',0) = \mathscr{H}^0_{d\bar{\mu}} P_2[\bar{\mu}\cdot\mu(t'')] \qquad [21]$$

where

$$\mathscr{H}^0_{d\bar{\mu}} = \sum_{j<i} b_{ij}(3I_{i\bar{\mu}} I_{j\bar{\mu}} - \boldsymbol{I}_i\cdot\boldsymbol{I}_j). \qquad [22]$$

$\mathscr{H}^0_{d\bar{\mu}}$ is of course just the "secular" part of $\mathscr{H}^0_d$, the part that commutes with $\bar{\mathscr{H}}_{\Delta}$. With this notation, for example, $\mathscr{H}^0_d \equiv \mathscr{H}^0_{dz}$. Thus, we obtain finally for the average Hamiltonian (excluding $\bar{\mathscr{H}}_{\Delta}$) putting [21] into [20]:

$$\bar{\mathscr{H}}^{00}_{DTR} = \bar{\mathscr{H}}^{00}_d = \mathscr{H}^0_{d\bar{\mu}} \bar{P}_2[\bar{\mu}\cdot\mu(t)]. \qquad [23]$$

As usual the bar denotes an average over the rf cycle:

$$\bar{P}_2(\bar{\mu}\cdot\mu(t)) = \frac{1}{t_c}\int_0^{t_c} P_2[\bar{\mu}\cdot\mu(t)]\,dt, \qquad [24]$$

where $\bar{\mu}$ is defined in [14] and $\mu(t)$ is the integrand. We prefer to leave [23] in the rotating frame since normal detection methods (*17*) correspond to measurements in this frame and not in the more suitable tilted frame along $\bar{\mu}$ (*14*).

Discussion

Equation [23] expresses a simple yet remarkable result. It says that no matter how complicated the cycle of rf excitation, if it is applied with a resonance offset fulfilling conditions 11(i)–(iii) then the average dipolar Hamiltonian is just the truncated Hamiltonian itself along an average axis in the rotating frame. This is depicted pictorially in Fig. 1. Obviously in a frame tilted (*14*) with its z axis along $\bar{\mu}$, $\bar{\mathscr{H}}^{00}_d$ is exactly proportional to [8]. In order to calculate this average Hamiltonian it is thus not necessary to calculate $\bar{\mathscr{H}}^0_{TR}$ in the intermediate step—we need only: (i) find $\bar{\mu}$ and write down $\mathscr{H}^0_{d\bar{\mu}}$ immediately and (ii) calculate $\bar{P}_2$ as in [24], so no manipulations are necessary on the spin variables. This fact, although rather obvious with a little reflection, is obscured in the original work (*11*) and with complicated cycles the manipulation of spin operators becomes unwieldy. The form of [23] allows a simple understanding of these experiments and permits us to draw more general conclusions (as we shall see for example in the discussion of spin locking). Of course in the event that we wish to enquire about the behavior at resonance ($\Delta\omega = 0$) this treatment is not valid and $\bar{\mathscr{H}}^0_{TR}$ must be calculated separately.

These results are easily generalized. If our interaction is not dipolar but is given, say, by a Hamiltonian $\mathscr{H}^0_n$ whose effective spin part transforms like the zero-order

component of an n'th rank irreducible tensor in the rotating frame, then under the same conditions:

$$\bar{\mathscr{H}}_n^{00} = \mathscr{H}_{n\bar{\mu}}^0 \bar{P}_n[\bar{\mu}\cdot\mu(t)]. \qquad [25]$$

For example the isotropic chemical shift treated by Ellett and Waugh (*10*) has a spin part which transforms like a first-rank irreducible tensor and indeed their average Hamiltonian is a special case of our results. There, however, $\bar{\mathscr{H}}_{TR}^0$ commutes with $\bar{\mathscr{H}}_{\Delta}^0$ (since I transforms like μ) and thus the result is independent of resonance offset.

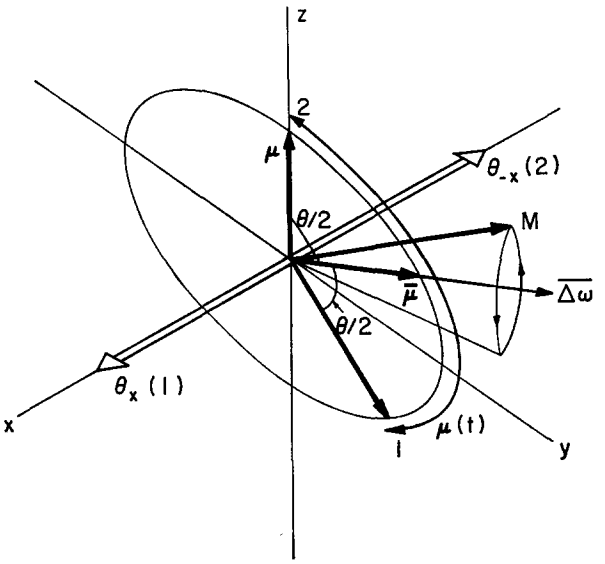

FIG. 1. Pictorial description of resonance offset averaging under the pulse sequence of Fig. 2(a). The pulses are imagined to be δ pulses ($t_w = 0$) and are depicted by arrows along x and $-x$ which nutate the unit magnetization vector μ alternately by angles $\theta°$ and $-\theta°$. Thus $\mu(t)$ switches between positions 1 and 2 and its average direction is given by the unit vector $\bar{\mu}$. The average offset field $\overline{\Delta\omega} = \cos(\theta/2)\Delta\omega$ points along $\bar{\mu}$ and thus any magnetization M will precess on the average about this axis with frequency $\overline{\Delta\omega}$. This gives rise to the scaling of chemical and inhomogeneous shifts. The factor $\bar{P}_2[\bar{\mu}\cdot\mu(t)]$ in Eqs. [23], [24] is simply evaluated for this sequence as $P_2(\cos\theta/2)$, so the average dipolar interaction is scaled by $\bar{P}_2[\bar{\mu}\cdot\mu(t)] = P_2(\cos\theta/2)$.

One nice feature of [23] is that it allows a quantitative comparison with experiment as, for example, in the work of Lee and Goldburg (*15*). In the case of irradiation at resonance, $\bar{\mathscr{H}}_d^0$ usually has some form different from $\mathscr{H}_d^0$ and lineshape comparisons are difficult to reconcile with theory. Thus, we have to date mostly satisfied ourselves with qualitative or semiquantitative conclusions, except in special cases. In the present case, however, arguments can be made more precise and quantitative.

Note that this treatment is not applicable to resonance offset experiments such as those of Lee and Goldburg (*15*) and Barnaal and Lowe (*16*), since there, requirement 11(ii) is violated ($t_c \sim t_{\Delta}$). In these cases the first transformation must be made not by $U_1(t,0)$ as in our case, but by the full effective field (*14*):

$$U_e(t,0) = \exp[-it(\mathscr{H}_1 + \mathscr{H}_{\Delta})].$$

In the present case the fact that H_1 is not exactly perpendicular to H_0 would be accounted for by correction terms in the expansion of $\bar{U}_R^0$, which are not considered here.

REPRESENTATIVE PULSE SEQUENCES

It now remains for us to specify the form of $\omega_1(t)$ in [7] and to write down some representative results. We select only simple examples to illustrate the general approach to application of the theory. Other examples will undoubtedly be investigated for fun by the interested reader.

Two-Pulse Cycle

Figure 2(a) shows the form of $\omega_1(t)$ for a phase-alternated two-pulse sequence. By inspection (see Fig. 1) we find immediately that $\bar{\mu}$ is in the $y-z$ plane and makes an angle of $\theta/2$ with the z axis. Defining the duty cycle δ by

$$\delta = 2t_w/t_c \qquad [26]$$

and using Eq. [23] we find trivially for a pure dipolar interaction

$$\bar{\mathscr{H}}_d^{00} = \mathscr{H}_{d\bar{\mu}}^0\{[3p_\delta(\theta)+1]/4\}$$
$$p_\delta(\theta) = (1-\delta)\cos\theta + \delta(\sin\theta/\theta). \qquad [27]$$

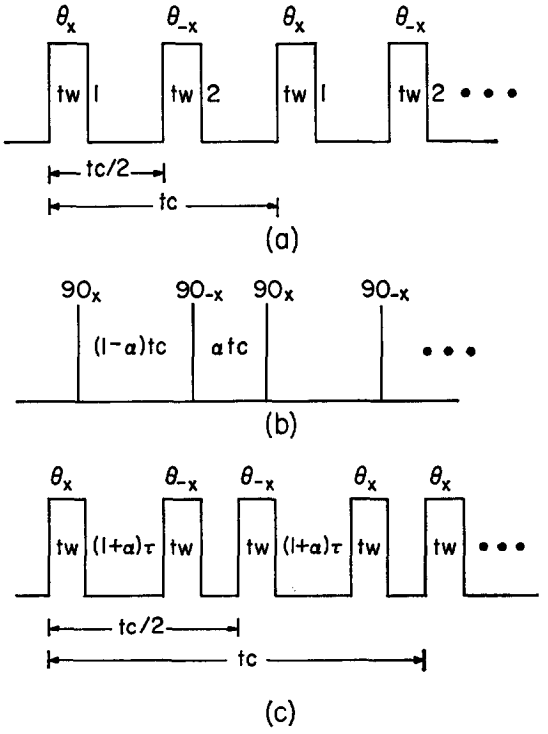

FIG. 2. Pulse sequences discussed in the text. Although not carried out here, these sequences may be symmetrized (*31*) by a redefinition of the cycle to eliminate some correction terms to the average Hamiltonian.

If there is an inhomogeneous or chemical shift term in the rotating frame Hamiltonian:

$$\mathscr{H}_c^0 = -\sum_i \sigma_{izz} I_{iz} \qquad [28]$$

where $\mathscr{H}_c^0$ is again a truncated form of the full chemical shift $\mathscr{H}_c$, then $\bar{\mathscr{H}}_{DTR}^{00}$ will contain another term given by:

$$\bar{\mathscr{H}}_c^{00} = \mathscr{H}_{c\bar{a}}^0 p_\delta(\theta/2) \qquad [29]$$

with p_δ defined in [27]; this is in agreement with previous results (*10*).

Line Narrowing

Figure 3 shows a calculated plot of $(3p_\delta(\theta) + 1)/4$ as a function of θ for several values of the duty factor δ. For $\delta < 0.75$ we see that $\bar{\mathscr{H}}_d^{00}$ can be made to vanish by an appropriate selection of θ and thus leads to a simple technique for line narrowing. For $\delta = 0$,

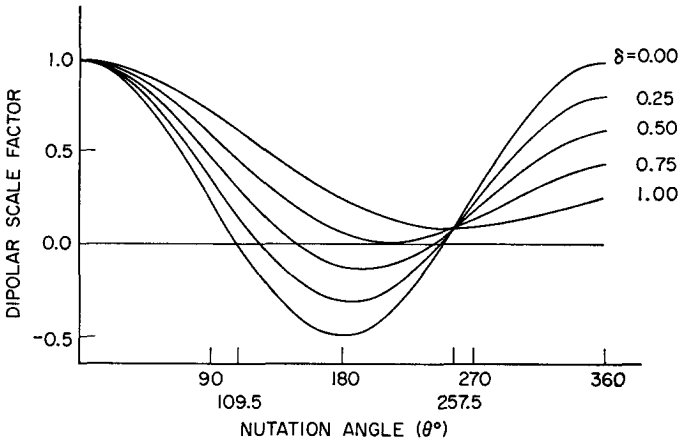

FIG. 3. Plot of the dipolar scale factor $\bar{P}_2[\bar{\mu}\cdot\mu(t)] = 1/4[3p_\delta(\theta) + 1]$ vs. θ for several values of the duty factor δ in the phase alternated pulse sequence [Fig. 2(a)]. The sequence produces line narrowing and is applicable for high resolution NMR in solids when $\bar{P}_2 = 0$, e.g., at 109.5° for $\delta = 0$ (the phase-alternated tetrahedral experiment). For $\bar{P}_2 < 0$ the Hamiltonian becomes "negative" yielding the conditions for time reversal.

i.e., δ pulses, we need $\theta = \theta_t$ where θ_t is the tetrahedral angle (109°28′); this is just the previously described PAT sequence (*11*). However, the present analysis shows that even for $\delta > 0$ the coupling can be made to vanish with $\theta > \theta_t$, thus eliminating the term in Eq. [21] of reference (*10*).

The fact that $\theta = \theta_t$ explains the limited line narrowing in Fig. 2 of the above work. With careful adjustment of $\theta > \theta_t$ decay times exceeding 1 msec for the ^{19}F nuclei in CaF have actually been attained for this experiment (*18*). Interestingly, it appears from Fig. 2 that employing $\delta \sim 0.75$ should be superior to the PAT experiment since the region of line narrowing is then markedly less sensitive to the exact value of θ and should thus be less sensitive to any inhomogeneities in the rf field. However, in this range $\overline{\Delta\omega}$ is also reduced so there is no large gain in cycle time. An experimental check of the full curves in Fig. 2 will be interesting and should provide an additional veri-

fication of this simple theory. Note that for any solution of $\tan\theta = \theta$, e.g., $\theta = 257.5°$, the line narrowing is predicted to be independent of the duty factor δ.

Magic Echoes

Magic echoes, which appear after homogeneous free induction decays in solids, were first reported by Rhim, Pines and Waugh (*8*). To remind the reader, magic echoes are produced in the following way: following the decay of magnetization due to $\mathscr{H}_d^0$, a strong rf perturbation is applied under which the effective Hamiltonian is given by $k\mathscr{H}_d^0$ with $k < 0$. This induces a negative time development which recalls the previous history of the spin system and produces an echo.

Looking at Fig. 2, we see that for small δ, we can make $3p_\delta(\theta) + 1 < 0$, i.e., $\bar{\mathscr{H}}_d^{00}$ "negative," thus yielding the necessary conditions for time reversal (*8*). The observation of magic echoes should provide verification for this aspect of the theory. These could be produced simply by applying a train of phase alternated pulses "sandwiched" between a pair of phase shifted ξ and $-\xi$ pulses as in the analogous on-resonance experiments (*8*).

Note that this is another manifestation of the simple form taken by the average Hamiltonian $\bar{\mathscr{H}}_{DTR}^{00}$. In a general pulse experiment, say an on-resonance phase-alternated sequence, the effective Hamiltonian has some other form except for special cases like 90° pulses (*3*) (*vide infra*) and time reversal becomes much more restricted.

Spin Locking

The form of $\bar{\mathscr{H}}_{DTR}^{00}$ allows another general conclusion. Since

$$[I_{\bar{\mu}}, \bar{\mathscr{H}}_{DTR}^{00}] = 0, \qquad [30]$$

we have all the prerequisites for spin locking of the $\bar{\mu}$ component of magnetization. We point out that [30] is the correct criterion to employ for spin locking; the presence of an average or mean H_1 field is neither sufficient nor a necessary condition as is still sometimes erroneously assumed.

We see, then, that the observation of $T_\parallel$ and $T_\perp$ (*20*) should be a general phenomenon in any resonance offset multiple-pulse experiment. If we start with the magnetization along an arbitrary axis in the rotating frame, we may separate it into components perpendicular to and parallel to $\bar{\mu}$. The perpendicular component will then precess about $\bar{\mu}$ and decay by spin–spin processes with a time constant $T_\perp = \bar{P}_2^{-1} T_2$ where $\bar{P}_2$ is given by [24] and T_2 is the normal transverse relaxation time. For $\bar{P}_2 \to 0$ the decay will of course be dominated by correction terms. The parallel component will be spin locked and will change only by spin–lattice relaxation in the rotating frame (*12*, *14*, *21–24*). The effects of spin–lattice relaxation are very interesting in these experiments and will be treated in detail elsewhere.

If the effective field along $\bar{\mu}$, i.e., in $\bar{\mathscr{H}}_\Delta$, is inhomogeneous (for example from an inhomogeneous H_0 or from inhomogeneous shifts as in a polycrystalline solid) then $T_\perp$ may be dominated by this inhomogeneity if $\bar{P}_2$ is small. This effect can be demonstrated quite dramatically by production of inhomogeneous rotary spin echoes (*25*) when $\bar{\mu}$ is at the magic angle (i.e., $\bar{P}_2 = 0$) as in the experiments of Rhim and Kessemeier (*26*) and Pines, Rhim and Waugh (*27*). In the latter experiment, the nature of the two

components of magnetization is shown quite clearly using the off-resonance four-pulse technique (*5*).

The simple behavior we have outlined above is a peculiar characteristic of the resonance offset experiment. If we enquire into the behavior of the spin system under the pulse sequence of Fig. 2(a) at resonance ($\Delta\omega = 0$) we find from [13]

$$\bar{\mathscr{H}}_d^0 = -\tfrac{1}{2}\mathscr{H}_{dx}^0 + \tfrac{3}{2}p_\delta(\theta)\sum_{i<j} b_{ij}[\cos\theta(I_{iz}I_{jz} - I_{iy}I_{jy}) - \sin\theta(I_{iz}I_{jy} + I_{iy}I_{jz})]. \quad [31]$$

In this case an analysis of the spin system response is difficult and comparison with the normal unperturbed behavior can be made only on the basis of moments of the decays. For example the second moments defined by (*28*)

$$\langle\omega^2\rangle_\mu = \frac{Tr(\bar{\mathscr{H}}_d^0, I_\mu)^2}{TrI_\mu^2} \quad [32]$$

are given for [31] by

$$\langle\omega^2\rangle_x = p_\delta^2(\theta)\langle\omega^2\rangle_0 \quad [33]$$

$$\langle\omega^2\rangle_y = \tfrac{1}{4}[p_\delta^2(\theta) + 2\cos\theta\, p_\delta(\theta) + 1]\langle\omega^2\rangle_0 \quad [34]$$

$$\langle\omega^2\rangle_z = \tfrac{1}{4}[p_\delta^2(\theta) - 2\cos\theta\, p_\delta(\theta) + 1]\langle\omega^2\rangle_0, \quad [35]$$

where $\langle\omega^2\rangle_0$ is the normal high field truncated second moment

$$\langle\omega^2\rangle_0 = -\frac{Tr(\mathscr{H}_d^0, I_x)^2}{TrI_x^2}. \quad [36]$$

For $\theta = 90°$, $\delta \sim 0$ we have the experiment of Waugh and Huber (*29*) which produces a prolonged decay only along the x axis as expected from [33]. As we have seen though, this picture changes drastically as we go off resonance.

We take this opportunity to note that [33] also gives the second moment of a spin echo decay (with constant δ) produced by a 90_x pulse followed by a θ_y pulse since this is one cycle of the appropriate pulse sequence. This important problem has been dealt with separately (*9*).

Ideal 90° Pulses

Since the simple properties of 90° δ-pulses have a special appeal and in fact most proponents of multiple-pulse NMR have been primarily obsessed with such pulses, we enquire here into the possibility of using them for experiments similar to those mentioned above. A general two-pulse sequence composed of such pulses is shown in Fig. 2(b) with α variable from 0 through 1. If this sequence is applied with the appropriate resonance offset then, from [23]

$$\bar{\mathscr{H}}_d^{00} = \mathscr{H}_{d\bar{\mu}}^0\left[1 - \frac{3}{2}\frac{\alpha(1-\alpha)}{\alpha^2 + (1-\alpha)^2}\right], \quad [37]$$

where $\bar{\boldsymbol{\mu}}$ is in the $y - z$ plane and

$$\boldsymbol{\mu}\cdot\bar{\boldsymbol{\mu}} = \alpha/[\alpha^2 + (1-\alpha)^2] \quad [38]$$

and therefore $\bar{\mathscr{H}}_d^{00}$ cannot be made to vanish for any real α. Thus using only 90° δ-pulses we conclude that we must resort to a cycle containing more than two pulses to achieve

line narrowing. It is interesting that the maximal line narrowing of 0.25 occurs at $\alpha = 1/2$ which gives just the pulse sequence of Waugh and Huber (*29*).

Four-Pulse Cycle

There are many possible four-pulse cycles. The most well-known to pulsed NMR spectroscopists is the four-pulse four-phase WAHUHA cycle (*5*). Here we treat a four-pulse cycle employing only *two* phases shown in Fig. 2(c). Defining δ as in [26] we find again using [23]:

$$\bar{\mathscr{H}}_d^{00} = \mathscr{H}_d^0\left[\tfrac{1}{2}(1-\alpha)(1-\delta) + \tfrac{1}{4}(1+\alpha)(1-\delta)(3\cos^2\theta - 1) + \frac{\delta}{4}\left(1 + \frac{3\sin\theta\cos\theta}{\theta}\right)\right] \quad [39]$$

which reduces for $\theta = \pi/2$ to

$$\bar{\mathscr{H}}_d^{00} = \bar{\mathscr{H}}_d^0[1 - 3\alpha(1-\delta)]/4. \quad [40]$$

For ideal δ pulses, $\delta = 0$, we see that we can achieve an effective line narrowing, $\bar{\mathscr{H}}_d^{00} = 0$, for $\alpha = 1/3$; this yields precisely the same timing as that of the WAHUHA cycle and has been verified experimentally, yielding decay times of 2 msec on the ^{19}F spins of CaF_2. Just as in this latter cycle the effects of finite pulse width can be compensated for. If we wish to retain 90° pulses then this is easily done by varying α (as long as $\delta < 2/3$) using [40]. The observed change in effective decay times going off resonance is quite marked for this pulse sequence. Magic echoes may be produced just as in the two-pulse cycle by making $\bar{\mathscr{H}}_d^{00}$ "negative."

SUMMARY

We have attempted to present a clear picture of the additional averaging effects produced by resonance offset fields in multiple-pulse NMR, and have illustrated this with some simple examples. In particular, the theory shows that behavior at, and far from resonance may be distinctly different, and that calculations made disregarding the resonance offset field lead to erroneous results (*30*). In addition, several uses of this phenomenon including line narrowing, spin locking, and magic echoes have emerged. We conclude by pointing out two other possible applications of this phenomenon in the future.

(i) Design of more efficient pulse sequences for line narrowing and magic echoes. The discussion in this paper has centered on zero-order effects, but there are equally profound higher-order effects which can be accounted for by the theory. These effects may in some cases outweigh the conclusions drawn from symmetry considerations alone in designing multiple-pulse experiments (*7*, *8*, *27*, *31*, *32*).

(ii) This type of experiment provides a simple means of producing effective static fields in the rotating frame with arbitrary directions and magnitudes, and with modified dipolar interactions, while being able to observe the magnetization between pulses. These facts give it an appealing potential for application to double-resonance experiments (*33*, *34*) which have stirred up some interest among chemists since their recent adaptations to high resolution NMR of dilute spins in solids (*35–37*).

ACKNOWLEDGMENT

We are grateful to J. D. Ellett, Jr. for many helpful conversations and for his aid with some aspects of the theory and experiments.

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